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Trichloroacetic acid assisted synthesis of gold nanoparticles and its application in detection and estimation of pesticide

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Abstract

Background: Many analytical methods are available for detection of methyl parathion in water but they are not handy for on-site analysis. An attempt has been made to utilize stable GNP for methyl parathion detection by sensing the peak at 400 nm generated due to the interaction between methyl parathion and GNP.

Methods: GNP was produced by reduction of chloroauric acid solution by trichloroacetic acid in alkaline medium in presence of CTAB. Sensor properties of GNP were studied by varying the concentration of methyl parathion in gold sol from 0 to 500 ppm.

Results and discussion: GNP stabilized by CTAB showed only one peak at 532 nm and one broad peak near 300 nm was observed for pure methyl parathion. But as soon as methyl parathion was added in the GNP solution, one new peak at 400 nm developed in addition to the other two peaks. More interestingly, a quantitative decrease of the absorbance at 532 nm of GNP and increase of the absorbance at 400 nm, the new peak, were observed when methyl parathion concentration increased from 10 to 500 ppm.

Conclusions: The UV-VIS measurement and TEM images confirmed that the surfactant capped GNP can act as a colorimetric sensor for detection and estimation of methyl parathion pesticide present in water in ppm level.

Keywords: Gold nanoparticles, Cetyl trimethyl ammonium bromide, Sensor, Detection of methyl parathion, Estimation of pesticide, Spectroscopy

Background

The exponential growth in research in gold nanoparticles has been mainly due to the following reasons (i) stability of gold nanoparticles, (ii) many relatively easy preparation methods, (iii) its role in nanoscience and nanotechnology. For preparation of gold nanoparticles, many different reducing agents and stabilizing compounds have been employed to control shape and size of the particles. When gold nanoparticles approach each other and aggregate, the colour changes from red to blue because of the shift of the surface plasmon band to longer wavelength. The distinctive colors of gold nanoparticles have inspired people for years to use them as sensors because of several advantages over conventional electrochemical sensors. The literature shows that the use of conventional analytical methods for detection of pesticide is getting replaced by sensors due to ease of application. The detection of pesticide residues is done using different biosensors (Airoldi et al. 2007). Several enzymes have been used in the development of electrochemical biosensor based on the inhibition mode of the enzyme for the determination of pesticides (Upadhyay et al. 2009). GNP based dipstick immunoassay was developed for the rapid detection of organochlorine pesticides such as DDT at nanogram level (Lisa et al. 2009). Along similar lines, in the present work we have developed a method for preparation of gold nanoparticles (GNP) using trichloroacetic acid as reducing agent in alkaline medium in presence of surfactant which acts as capping agent. This surfactant capped GNP has been used as colorimetric sensor for detection and estimation of pesticide (methyl parathion) present in a sample. Methyl parathion is chosen because it is a

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highly neurotoxic agricultural chemical that is used extensively worldwide to control a wide range of insect pests. Its residue in the soil causes pollution in the environment and poses a risk to human health. We have employed cetyl trimethyl ammonium bromide (CTAB) capped GNP as sensor and the change in UV-Visible spectra was monitored when pesticide (methyl parathion) was added at ppm level.

Many analytical methods are available for detection of methyl parathion in water. The common analytical techniques include HPLC (high performance liquid chromatography) with UV detection (Huang et al. 2002), GC-Mass spectrometry (Ferrer et al. 2005; Garcia-Reyes et al. 2007), GC/ECD (gas chromatography coupled with electron capture) (Bicchi et al. 2003; Brito et al. 2002), GC/FPD (gas chromatography coupled with flame photometry) (Berijani et al. 2006), GC/FID (flame ionization detection) (Pinheiro & Andrade 2009). All these methods are very sensitive but each one requires its unique method for sample preparation and above all, they are not handy for on-site analysis. These are mainly applied in laboratory settings and restrict rapid analysis under field conditions. At the same time they are expensive and time consuming. For this reason, an attempt has been made to utilize stable GNPs for methyl parathion detection. The nano colloidial GNPs could detect methyl parathion by forming bond using sulphur present in methyl parathion and thereby generating a new peak near 400 nm. The height of this peak is proportional to the concentration of methyl parathion and this makes for a ready means of estimating the pesticide concentration.

Methods

Preparation

Trichloroacetic acid, chloroauric acid, cetyl trimethyl ammonium bromide, all AR grade, were purchased from Sigma-Aldrich Chemical Ltd. Sodium hydroxide and methyl parathion were purchased from Merck. Double distilled de-ionized water was used in all experiments.

GNP was produced by reduction of chloroauric acid solution by trichloroacetic acid in alkaline medium in presence of CTAB. The pH was varied during reduction by adding different amounts of NaOH solution.10 ml of 3 × 10-3(M) trichloroacetic acid solution was added to an equal volume of the same concentration of alkaline CTAB. The mixture was cooled in ice cold water. Then 7 ml of 3 × 10-3(M) aqueous chloroauric acid was added drop wise with continuous stirring. The mixture was cooled for 10 minutes and then it was heated at 850C for 1 hour. The colour of the solution gradually changed from yellow to violet to reddish violet. The reddish violet colour indicated the formation of gold nanoparticles (GNPs).

Characterization

The absorbance spectra of the GNPs were analyzed by using a 'SHIMADZU' UV 1800 spectrophotometer and TEM images were taken using JEOL-JEM 2100 high resolution transmission electron microscope (HR-TEM). Samples for the TEM studies were prepared by placing a drop of the aqueous suspension of particles on carbon-coated copper grids followed by solvent evaporation under vacuum. The crystalline nature of the GNPs was examined using X' Pert-PRO model (Analytical Holland) X-ray diffractometer.

Sensor properties of GNP were studied by varying the concentration of methyl parathion in gold sol from 0 to 500 ppm. 250 μl of solution containing different concentrations of methyl parathion was added to 5 ml of "as prepared" GNP. The sol was heated for 5 minutes with stirring. The reddish violet color changed into yellow. The intensity of yellow colour gradually increased with increase of pesticide concentration.

Results and discussion

Optimization of GNP preparation

GNP displays optical properties due to the presence of surface plasma resonance (SPR) band. For spherical gold particles the SPR occurs nearly at 540 nm. Small shifts in the SPR band occur perhaps due to the changes in the dielectric properties of the medium of the GNP or due to the specific adsorption of materials on the surface of the gold particle. Mie theory is generally used to explain the shifts in the SPR band (Mie 1908; Creighton & Eadon 1991). According to this theory, shifts in SPR may also occur when particles geometry changes from spherical to some other shapes. In the present work, the GNP as prepared produces SPR band at 532 nm. We have observed that the pH and concentration of the surfactant have important roles in the formation of GNP. Hence the effects of pH and concentration of CTAB were investigated thoroughly. To optimize the pH of the solution it was varied from 7.0 to 11.0 during the reaction. When the pH is higher than 8.0 and lower than 10.5, the GNP solution was stable for more than six months. However, if the pH is lower than 8.0, the precipitation occurred within several hours. One interesting observation should be pointed out that though pH and CTAB concentration have effect on the stability of the GNP formation yet the SPR band was fixed at 532 nm in all cases. From the extinction spectra (Figure 1A) it is seen that maximum absorbance of GNP peak i.e. 532 nm peak is found at pH 9.5. Furthermore, it has been observed that 3 × 10-3 (M) concentration of surfactant produced most stable sol, though 5 × 10-3(M) concentration produced higher extinction coefficient of 532 nm peak (see Additional file 1: Figure S1B). At higher concentration of the surfactant, precipitation of the sol occurred. That is why in our experiments we

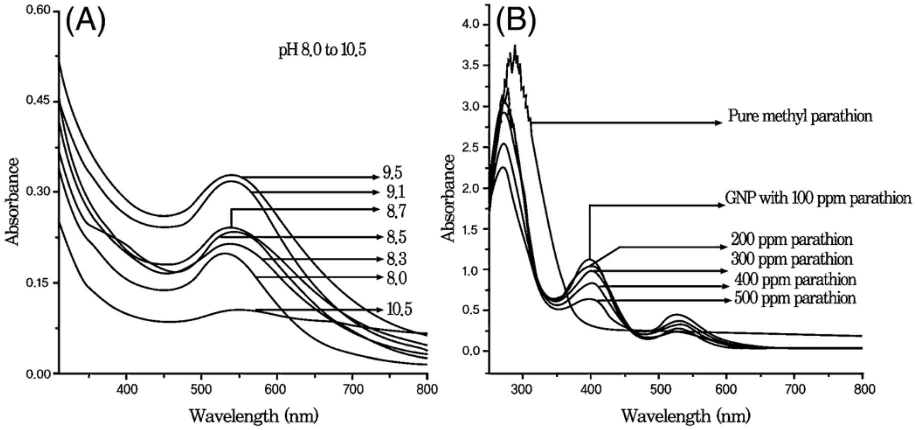


Figure 1 **UV–vis spectra of (A) GNP at different pH and (B) Pure methyl parathion and GNP with different concentrations of methyl parathion.**

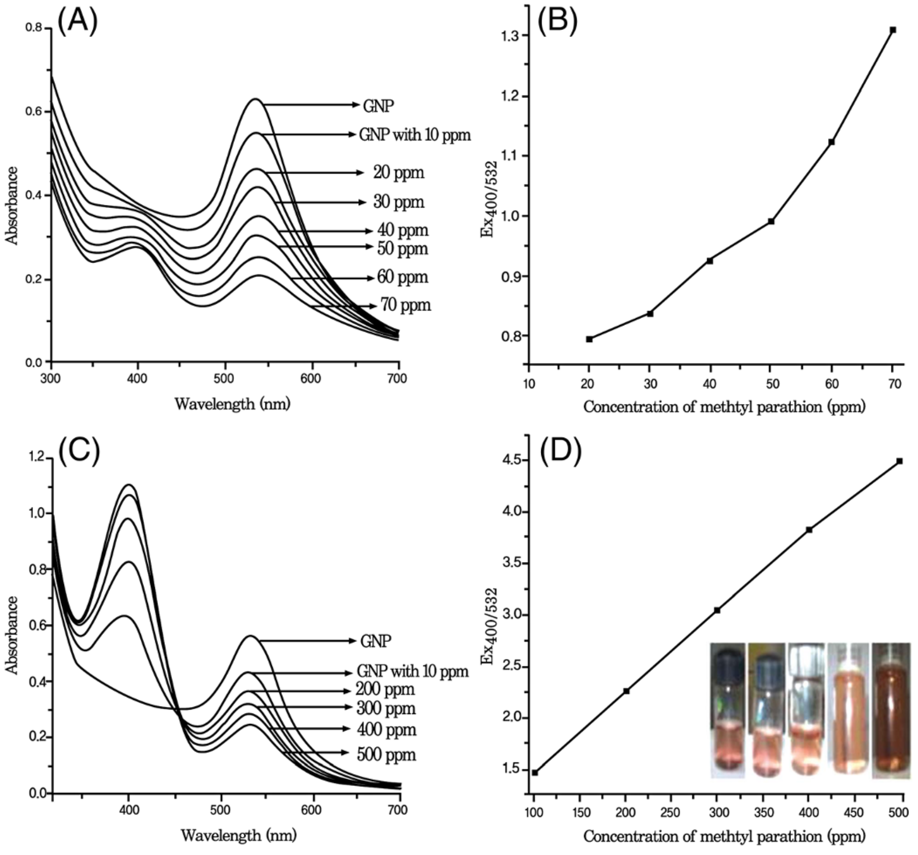
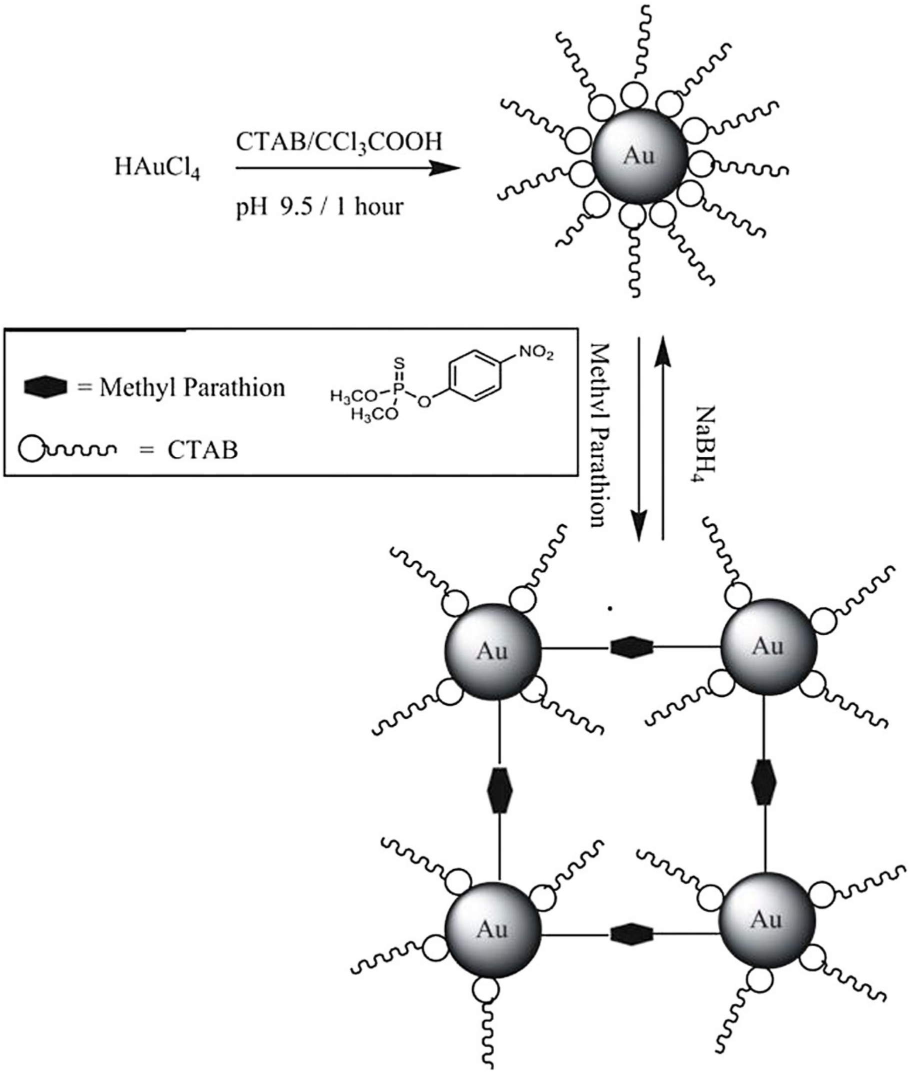


Figure 2 **UV–vis spectra of GNP and GNP with various concentrations of methyl parathion (A) 10 to 70 ppm (C) 100 to 500 ppm and corresponding changes of absorption coefficients (Ex 400/532) with various concentrations of methyl parathion (B) 10 to 70 ppm (D) 100 to 500 ppm.** 2(D) (inset): digital photographic images of color changes due to addition of methyl parathion.



Scheme 1 Strategy for the formation, aggregation and segregation of GNP.

have used 3 × 10-3(M) CTAB with equi-molar chloroaruric acid at pH 9.5 to get most stable GNP.

The change in the absorbance spectra due to the increasing methyl parathion concentration from 0 to c depicted in Figure 1(B), 2(A) & (C).

GNP stabilized by CTAB shows only one peak at 532 nm while pure methyl parathion shows one broad peak near 300 nm. But as soon as methyl parathion is added in the GNP solution, one new peak at 400 nm starts developing in addition to the other two peaks. More interestingly, a quantitative decrease of the absorbance peak at 532 nm of GNP and increase of the absorbance at 400 nm, the new peak, are observed when methyl parathion concentration increases from 10 to 500 - ppm. The appearance of the new peak near 400 nm might be due to the bond formation between phosphorothioate group present in methyl parathion and the GNP. A control experiment shows that no such peak is obtained when methyl parathion is added in pure chloroauric acid (see Additional file 1: Figure S2B). It is well known that many compounds containing sulphur are specifically being employed for functionalization of GNP through ligand exchange reaction.

In recent years, mercaptopropionic acid (Huang & Chang 2007), mercaptoundecanoic acid (Templeton et al. 1998), glutathione (Chai et al. 2010), etc. were used for this purpose. From the chemical structure of the pesticide we can also predict that phosphorothioate group may definitely help the functionalization of GNP due to which the new peak appears near 400 nm (Figure 1(B), 2(A) & 2(C)).

The probable mechanism for bond formation and aggregation of sol particles are elaborated in Scheme 1.

The absorption coefficient ratio (the ratio of absorption coefficient of 400 and 532 nm peaks, Ex 400/532), which measures the changes in absorption peaks due to the addition of various concentrations of pesticide, has been investigated thoroughly. The ratio increases with the increase of concentration of the pesticide. This phenomenon suggests that more the phosphorothioate group more is the functionalization of GNP up to a certain concentration of pesticide. A calibration curve between the absorption coefficient ratios versus concentration of pesticide can help one to estimate quantitatively the presence of methyl parathion in a sample at ppm level (Figure 2(B) & 2(D)).

The TEM measurements of GNP produced at around pH 9.5 show almost spherical particles of different sizes (Figure 3(A)). The capping of the hydrophobic part of CTAB on GNP shows a layer surrounding the gold particle. In presence of methyl parathion, the size, shape altogether changes drastically and a completely different look with an exciting feature is observed (Figure 3(B), 3(C) & 3(D)).

It appears that restructuring of GNP occurs after addition of methyl parathion. Spherical particles become spheroidal and agglomeration of particles is observed. It is likely that the surface of the GNP forms an Au-S co-ordination bond (this can happen as the sol is being heated after addition of methyl parathion) and some methyl parathion molecules get adsorbed on the Au surface by replacing CTAB. As methyl parathion is anionic in alkaline medium, its adsorption on the GNP surface lowers the surface charge and thus they agglomerate and the interesting particle clustering is observed. Each cluster has an average size of 50 nm. These clusters segregate to give back GNP reversibly when reduction is performed with $NaBH_4$ (Scheme 1 and Figure 4).

Detailed studies are in progress to know the exact chemical nature of the bond formed between GNP and methyl parathion. A recent review discusses the recent progress in understanding of molecular structure of the gold-sulfur interface in thiolate-protected gold surfaces and interfaces from the viewpoint of theory and computations, with connections to relevant experiments (Hakkinen 2012). Though thiolate group is not present in this work, phosphorothioate group may be responsible for the Au-S interaction. We are also interested to know what sort of interactions is actually taking place on the GNP surface with methyl parathion so that new peak develops at 400 nm. To investigate this bonding XRD and FTIR have been employed. The XRD

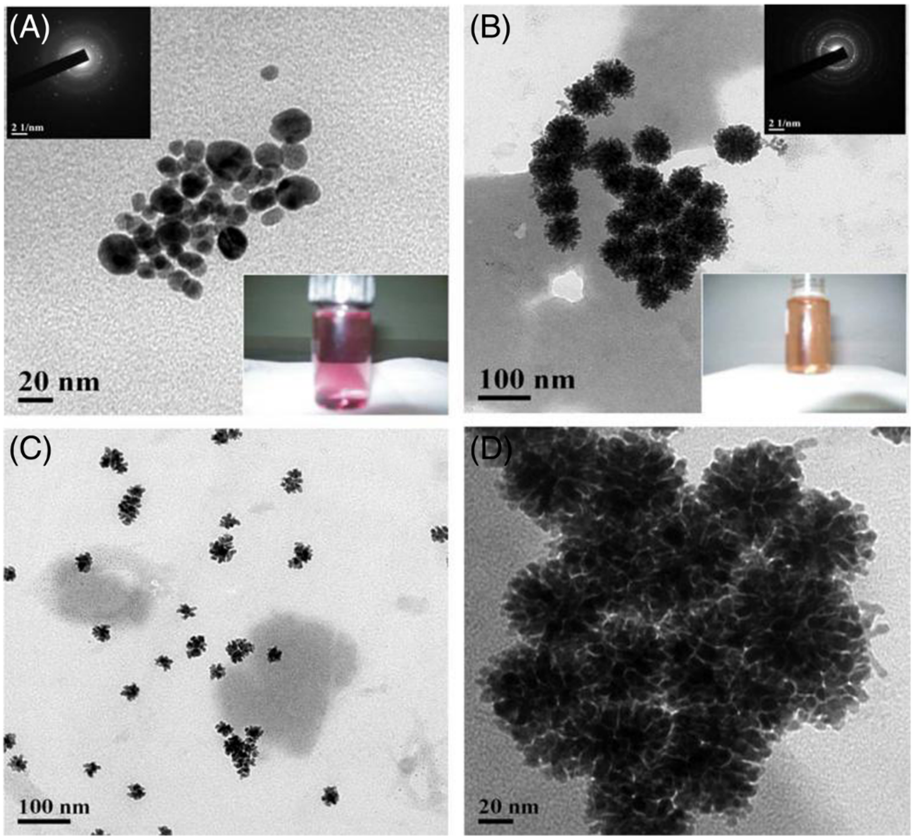


Figure 3 TEM micrographs of GNP (A) before and (B), (C) & (D) after addition of methyl parathion.

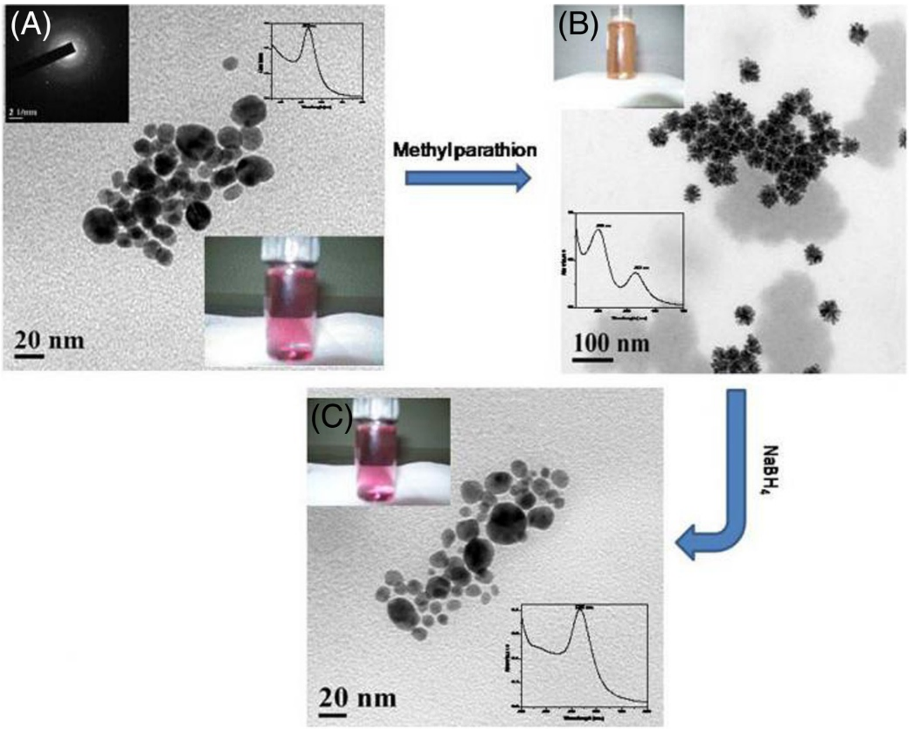


Figure 4 **A strategy of aggregation of GNP (A) due to reaction with methyl parathion (B) and segregation of GNP by reduction with NaBH$_4$ (C).**

pattern of the GNP shown in Figure 5(A) indicates the face centered cubic (fcc) structure of the bulk gold having peaks at 38.175o, 44.525o, 64.675o, 77.675o and 81.825o corresponding to (111), (200), (220), (311) and (222) planes, respectively. In literature we find Au2S shows peaks near 31o, 35.5o, 51.5o, 61.5o and 65o in XRD (Kuo & Huang 2008). The XRD spectrum of the GNP after reaction with methyl parathion are shown in Figure 5(B) and it is visible that the spectrum has all peaks due to Au as well as some additional peaks at 50.5 o, 60.06o and 64.5 o which may be attributed to the Au-S co-ordination bond.

FTIR spectra (Additional file 1: Figure S5) of the GNP before and after addition of methyl parathion show almost no changes in the peak positions (slightly shifted). The peaks are mainly due to the CTAB present in the system (Liu et al. 2007). The comparison of the spectra shows the appearance of new peaks near 1480 cm-1 and 853 cm-1 which we are unable to assign. More work is needed to understand the

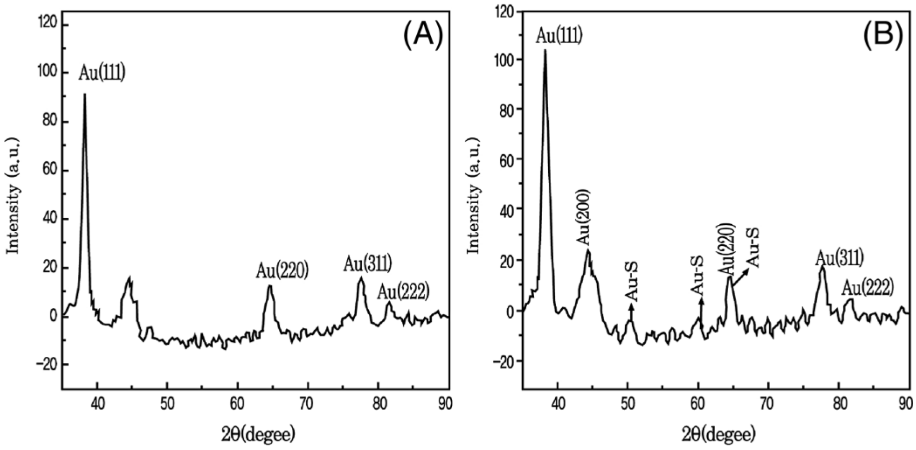


Figure 5 **XRD of GNP (A) before and (B) after addition of methyl parathion.**

nature of the bond which may be crucial for some applications of gold based nanoparticles for some other purposes.

Conclusion

We have employed CTAB capped GNP as sensor and the change in UV-Visible spectra was monitored when methyl parathion was added at ppm level. The UV–VIS measurements and TEM images confirm that the surfactant capped GNP can act as a colorimetric sensor for detection and estimation of methyl parathion pesticide present in ppm levels by utilizing the bonding between GNP and phosphorothioate group of the pesticide. Agglomeration of the GNPs occurs due to the adsorption of methyl parathion on the GNP surface, and hence the interesting particle clustering is observed. These clusters segregate to give back GNP reversibly when reduction with $NaBH_4$ is done.

Supporting information

UV–vis spectra of GNP formation with varying time and concentrations of chloroauric acid and CTAB result of control experiment with pure chloroauric acid, strategy and some TEM photographs for aggregation and segregation of GNP. These materials are available free of charge on the Web at http://www.jsac.or.jp/analsci/.

Additional file

Additional file 1: Figure S1. UV-Vis spectra of GNP formation with varying concentrations of (A) chloroauric acid (B) CTAB. **Figure S2.** UV-Vis spectra of GNP formation varying time of reaction from 20 minutes to 2 hours keeping chloroauric acid concentration constant at 3×10 -3 (M) and (B) Absorption spectra of pure chloroauric acid in presence of methyl parathion at various concentration. **Figure S3**. Different TEM micrographs of GNP (A) & (B) and GNP after reaction with methyl parathion (C) & (D). **Figure S4**. UV representation of aggregation of GNP (A) due to reaction with methyl parathion (B) and segregation of GNP by reduction with $NaBH_4$ (C). **Figure S5**. FTIR spectra of (A) GNP and (B) GNP with methyl parathion.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

GB carried out the experiment. GB and SM drafted the manuscript. JKL guided the research and modified the manuscript. All three authors read and approved the final manuscript.

Authors' information

JKL is Associate Professor and Head of Department of Chemistry, Midnapore College, West Bengal, India. GB and SM are research scholars of this Department.

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